Coking Behaviour of Cr-ZSM-5 in Catalytic Decomposition of Ethyl Acetate and Benzene Pollutants In Air Stream

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ABSTRACT: *The behaviour and physicochemical characteristics of coke formed during ethyl acetate and benzene decomposition are reported. Coked Cr-ZSM-5 was prepared by exposing the catalyst to 32,000 ppm of both organics at GHSV of 3,800 hour^{-1} at 400°C for 12 hours. Elimination of micropores, enlargement of pores and loss of crystallinity of the catalyst of between 65 to 85 % depending on coking conditions were demonstrated. Reduced catalytic activity caused by coking was attributed to partial blocking of active sites. Infra red spectra showed that coke preferentially accumulated around extraframework acid sites and Bronsted acid sites. The rate of coking was found to be faster with ethyl acetate and dry feed. Benzene decomposition produced coke of more polyaromatic nature. Water vapour enhanced coke formation from ethyl acetate reaction due to increased surface hydroxyl concentration while with benzene less coking tendency was demonstrated. Softer coke was formed at temperatures below 300°C and an increase in the difficulty of coke oxidation was observed as the reaction temperature increased. The stability of Cr-ZSM-5 catalytic activity was due to preference of coke to form in the extraframework mesopores of the zeolite rather than in the micropores that host most of active sites.*

INTRODUCTION

Volatile organic compounds (VOCs) are an important class of air pollutants, emitted from many industrial processes and transportation activities and catalytic combustion is one of the most promising technologies for the elimination of these substances in air due to its definitive character and save of energy (Becker and Förster, 1998). However, catalyst deactivation stands as the main drawback in this process. Catalyst deactivation in VOC decomposition process can be attributed to many reasons, of which the most dominants are coking and structural changes (Dégé et al., 2000). There are numerous investigations on the effect of coke deposition on catalytic activity in hydrocarbon reactions (Antunes et al., 2001 ; Sahoo et al., 2001 ; Ivanov et al., 2002). In many cases, poisoning of the active sites or blocking of pores were discussed. However, reports on types and characteristics of coke, and how they relate to the catalytic reactor operational conditions are quite scanty. Factors like reaction temperature and humidity in the feed are important since they determine the types of chemical and physical coking mechanisms involved.

In this study, ethyl acetate and benzene were used as VOC model compounds based on differences in their chemical nature and role in environmental VOC pollution. Chromium is the most active metal among the transition metals (Zuhairi et al., 2002) and it was selected to be metal exchanged with ZSM-5 zeolite to produce a catalyst of high activity, high stability and less coking tendency. The main objectives of this paper are to investigate the dependence of Cr-ZSM-5 activity with coking and, the relationship between reaction temperature and feed water vapour with characteristic of coke accumulated.

EXPERIMENTAL PROCEDURES

- Preparation of Cr-ZSM-5

Chromium exchanged ZSM-5 (Si/Al=240) was prepared in two steps. In the first step, NH_4^+ exchange of H-ZSM-5 (Si/Al=240) was performed in 2.25 M of NH_4Cl solution for 6 hours. The metal exchange step was done in acidified (to pH 4) aqueous $Cr(NO_3)_3$ solution at 0.086 mol/l, for 6 hours followed by filtration, drying and calcination at 500°C for 6 hours. Before used in the reactor, the catalysts were palletized, crushed and sieved between 0.25-0.30 mm.

- **Experimental Setup**

The preparation of coked Cr-ZSM-5 samples and catalytic activity test was performed in an 11 mm i.d. glass reactor charged with 0.2g of zeolite catalysts (Figure 1). VOC-laden air stream as feed to the reactor was generated by bubbling nitrogen gas through the VOC saturators. Water vapour in the feed was generated by passing the same gas through water saturator and another flow of high purity air was used to make up the total flow rate to give the desired GHSV. The accurate control of flow rate was achieved by means of Aalborg (AFC 2600) mass flow controllers. In order to prepare coked Cr-ZSM-5 samples, feeds containing 32,000 ppm of ethyl acetate and benzene were passed through the reactor at reaction temperature of 400°C and GHSV of 3,800 hour^{-1} for 12 hours. In the activity study, the reactor was operated at GHSV of 32,000 hour^{-1}. The feed and product gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph. Porapak Q column was used for separation of carbon dioxide and organic components while the separation of carbon monoxide was achieved by means of a Molecular Sieve 5A column.

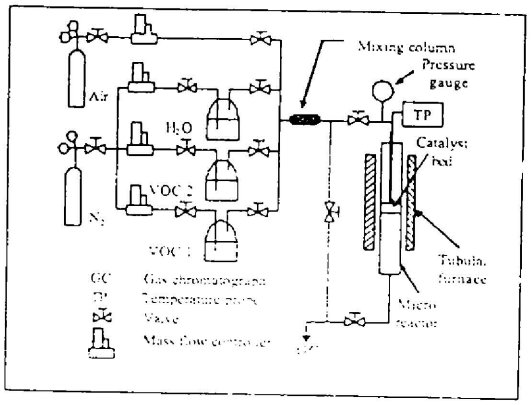

Figure 1. Schematic diagram of the reactor system used in this study.

The catalyst samples were characterized for surface characteristics using Quantachrome Autosorb-1, metal loading using Shimadzu AA-6650 atomic absorption spectroscopy, and crystallinity using Siemens D2000 X-ray diffractometer. Thermogravimetry experiments on coked Cr-ZSM-5 were performed using Perkin Elmer TGA7 thermogravimetry analyzer under pure oxygen flow at 20 ml/min and at temperature ramping rate of 10°/min. Infrared spectroscopy characterization of coked samples was performed using Perkin Elmer 2000 FTIR system. In acid sites characterization, prior to scanning with FTIR the samples were adsorbed with pyridine and desorbed at 150°C for 1 hour.

RESULTS AND DISCUSSION

- **Characteristics of the catalysts**

The characteristics of CrZSM-5 catalyst prepared are as shown in Table 1. Chromium exchange was found to cause 4 % drop in relative crystallinity mainly attributed to heat treatment in during preparation. Significant loss of crystallinity was observed after treatment with ethyl acetate, but with benzene, the loss was slightly lower. The inclusion of 9,000 ppm of water in the feed was shown to further speed up loss of crystallinity. Chromium exchange and coking were found to cost the catalyst about 22-32 % of its micropore area while mesopore area and mean pore diameter increased. Coking resulting from ethyl acetate seemed to be more severe compared to the effect from exposure to benzene under the same conditions.

Table 1. Characteristics of Cr-ZSM-5 catalysts as compared to its parent H-form.

Characteristics	Catalyst					
	H-ZSM-5	Cr-ZSM-5	[b]Cr-ZSM-5(EAc)		[c]Cr-ZSM-5(Bz)	
			Dry	Humid	Dry	Humid
S_{BET} (m^2/g)	393	366	326	314	338	320
Micropore area (m^2/g)	321	272	183	198	213	195
Mesopore area (m^2/g)	72	94	143	116	125	125
Mean pore diameter (Å)	22.5	22.8	23.2	23.8	23.0	23.4
Chromium loading (%)	-	0.98	0.98	0.98	0.98	0.98
[a]Relative crystallinity (%)	100	96	78	65	85	73

[a]Relative to parent ZSM-5
[b]Exposed to 32,000 ppm ethyl acetate for 12 hours at 400°C.
[c]Exposed to 32,000 ppm benzene for 12 hours at 400°C.

- **Activity study**

Coking of Cr-ZSM-5 was observed to deactivate the activity of the catalyst as clearly depicted in Figure 2 (a). The effect was more significant at lower temperatures especially between 200° to 350°C. As noted in the figure, ethyl acetate was more reactive over Cr-ZSM-5 compared to benzene. This was due to the presence of carbonyl group in this substance to provide effective host for molecular fission compared to stabilization due to resonance effect in aromatic ring in benzene. Clear drop in carbon dioxide yield with coked catalyst was also observed as shown in Figure 2 (b).

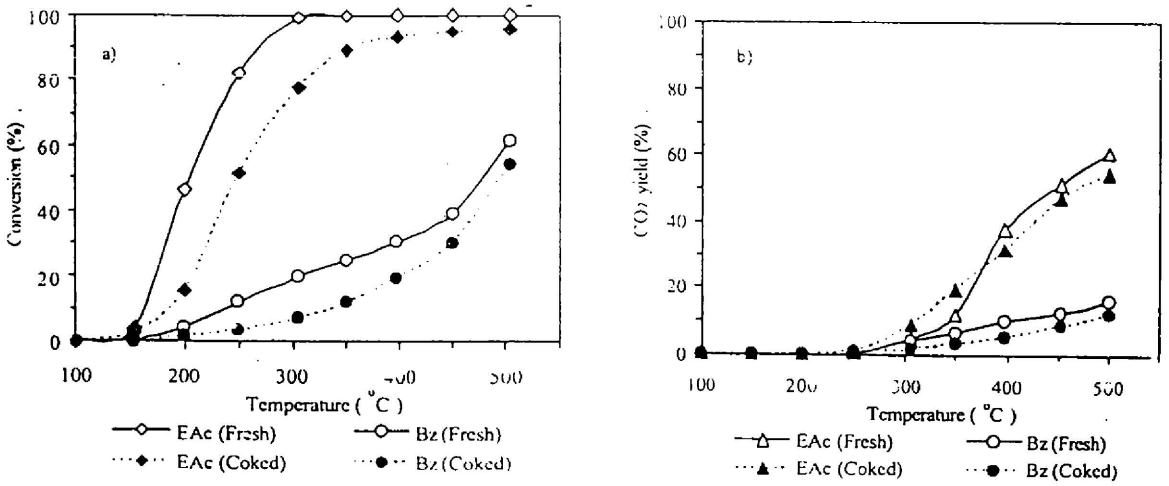

Figure 2. Effect of coking on ethyl acetate (EAc) and benzene (Bz) decomposition. a) effect on conversion, and, b) effect on carbon dioxide yield. (GHSV=32,000 hour^{-1}, C_{VOC}=2,000 ppm, coking conditions : 32,000 ppm of respective VOC for 12 hours at 400°C).

Coke formation is strongly dependent on the zeolite structure, reaction conditions and on the nature of the reactants. Partial blockage of ZSM-5 channel system caused some of the active sites that lined the channel inaccessible. Earlier study concluded that medium pore zeolite like beta or zeolites with channel system of different sizes like mordenite accumulated more coke, and hence, more deactivated. The less coking tendency of Cr-ZSM-5 was ascribed to interconnected channels of similar dimension (5.5Å) found in this material. Figures 2 suggest that the catalytically active sites that involved in VOC decomposition process were minimally affected by coking as only slight drop in activity with coked Cr-ZSM-5 at higher temperatures was detected. Thus, it can be inferred that coke preferentially deposited on different site that would not interfere with the organic decomposition process. Reduced activity at high temperatures could be attributed to pore mouth blocking and/or blocking of active sites adjacent to coked sites. Meanwhile, low activity of coked CrZSM-5 at lower reaction temperatures could be the consequence of diffusion limitation as the feed molecules were less mobile at these temperatures. The effect of coking on carbon dioxide yield was attributed to less active sites available for the organics conversion that resulted in lower yield.

- **Effect of water vapour**

Results as shown in Figure 3(a) suggest the complexity of coke composition on coked Cr-ZSM-5 with strong absorption in the wave number range of 1,400 to 3,100 cm^{-1} ascribed to carbon-carbon stretching absorptions. The absorption in this region was stronger in Cr-ZSM-5 catalysts coked by ethyl acetate. It could be due to more C=C bond present in the coke as this bond produced more intense and broader absorption bands than C–C or C≡C. The presence of graphite coke on this catalyst could not be ruled out (Sahoo et al., 2001). After catalyzing benzene decomposition, the stretching of absorption bands of aromatic C–H bonds was detected in the region of 3180 to 2980 cm^{-1} signifying polyaromatic nature of the coke. Strong absorption band at 3,600 cm^{-1} was ascribed to strong acid sites resulting from the interaction between extra frame work aluminium species with the zeolitic hydroxyl groups. Decreasing intensity of this broad band upon coking was an indication of preferential formation of coke on these sites. Qualitatively estimation on the amount of coke accumulated on these sites indicated that more coke formed upon exposure to ethyl acetate and in the absence of water molecule as co-feed.

Infra red spectra with chemisorbed pyridine as probe molecule characterized another two types of acid sites sitting on Cr-ZSM-5 catalyst (Figure 3(b)). Peak at 1446 cm^{-1} was attributed to pyridine attached to true Lewis acid sites. These sites were either occurred as threefold-coordinated aluminium or silicon and extra-framework aluminium-containing species such as AlO^{+}. The absorption occurred at 1545 cm^{-1} belonging to pyridinium ions (PyH^{+}) was used as an indicator of the

presence of acidic hydroxyls or better known as Brønsted acid sites on the external and internal surface of zeolite crystallites. Peak at 1440 cm^{-1}, indicative of interaction between pyridine and metal cations was not observed, probably due to overlapping with Lewis acid sites. Figure 3(a) suggest Brønsted acid sites were the stronger acid sites as at Si/Al ratio of 240, the number of Brønsted acid sites was simply outnumbered by Lewis acid sites. Upon coking with ethyl acetate in dry condition, significant elimination of Brønsted acid sites was observed but the effect on Lewis acid sites was minimal. In humid condition, the effect on Brønsted acid sites was not as severe. The same trend was also observed with benzene but relatively more Brønsted acid were sites still available after 12 hours of coking process.

The accumulation of coke on Cr-ZSM-5 seemed to be concentrated around stronger acid sites found on the surface of the catalyst. These sites might have been deactivated within a short period due to coke formation and once the highly strong acid sites of enhanced active nature get deactivated, the rate of coke formation and the nature of coke formed will depend on the density of remaining acid sites present in the catalyst (Antunes et al., 2001). Thus, it can be inferred that the nature of coke formed does not depend on the strength but on the density of the acid sites. This result also suggested that Lewis acid sites had no or little role in coke formation during the decomposition of ethyl acetate or benzene molecules.

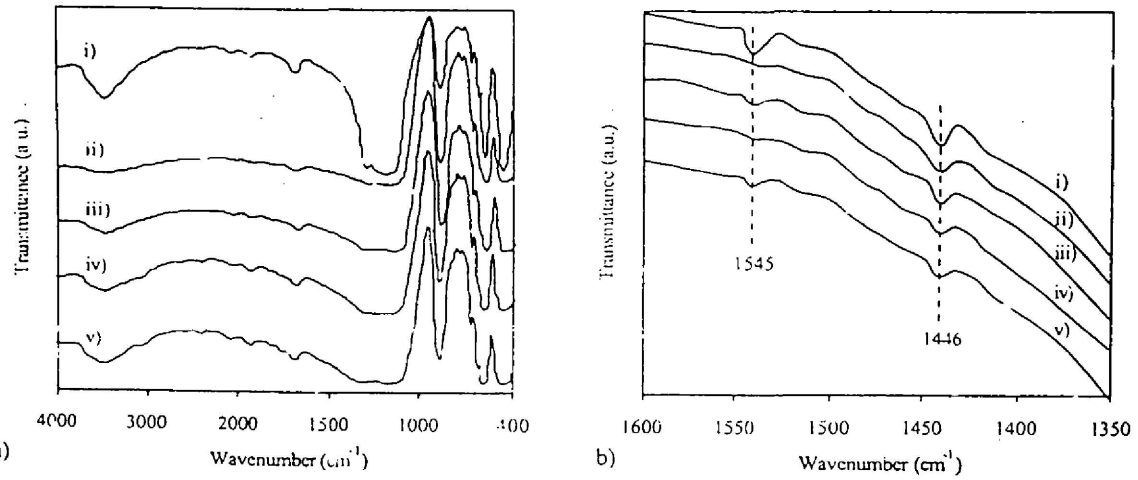

Figure 3 Infra red spectra of Cr-ZSM-5 catalyst a) without pyridine chemisorbed, and b) with chemisorbed pyridine. i) Fresh Cr-ZSM-5, ii) EAc (dry), iii) EAc (humid), iv) Bz (dry) and v) Bz (humid).

The olefinic/aromatic nature of the coke is very closely related to the types of molecule involved in the coking process and acidity of the catalyst. It is already established that the aromatic content of coke mainly depends on the hydrogen transfer ability of the acid sites present in the zeolite, which ultimately depends on the density of acid sites. The dehydrogenation reactions of cyclic hydrocarbon like benzene and higher olefins were reported to mainly occur via bimolecular reactions (Ivanov et al., 2002). Thus, the availability of two adjacent acid sites (high density of acid sites) is a necessary factor for bimolecular reactions to occur.

Results of thermogravimetry experiments on fresh and coked Cr-ZSM-5 catalyst samples, as depicted in Figure 4 reveal that there were two general groups of coke formed on the catalyst. The softer coke, mainly built up of polyaromatic hydrocarbon molecules with three or four conjugated cycles (Antunes et al., 2001), oxidized easily below 250°C. It accumulated preferentially on silanols on the extraframework phase, in defects, mesopores and on the external surface of the zeolite (Sahoo et al., 2001). The oxidation of harder coke fraction, mainly made of oxygenated polyaromatic compounds (Antunes et al., 2001), started to take place from around 500°C until complete oxidation above 650°C. Significant amount of relatively softer coke formed upon ethyl acetate coking as sharp drop in sample weight demonstrated by the sample below 200°C. Decomposition of ethyl acetate was also found to cause more coking of the catalyst but benzene decomposition produced relatively softer coke. Feed stream humidified by 9,000 ppm of water vapour was found to cause the catalyst to accumulate more coke during the decomposition of ethyl acetate, but the reverse was observed in the case of benzene. The difference in the hardness of the coke in dry and humid stream was not clearly distinguishable. The harder portion of the coke was oxidized between 500° to 650°C for ethyl acetate but it started at about 50°C lower for benzene as indicated by sharp drop in the sample weight in this region.

The effect of water molecule in the feed on the overall accumulation of coke was dictated by two mechanisms. First, it competed with organic molecules for adsorption on active sites to consequently lower the conversion of these organics. Therefore, due to less reaction took place, less coke formation resulted as observed in the case of humid ethyl acetate.

Secondly, it increased the concentration of surface hydroxyls on the catalyst that upon hydrolysis formed Brønsted acid sites that responsible for coke accumulation. This mechanism explained higher coking tendency during the decomposition of benzene in the presence of water as co-feed. Sinquin et al. (2000) claimed that water molecules could cause the transformation of Lewis acid sites into Brønsted acid sites but this phenomenon was not observed in this result.

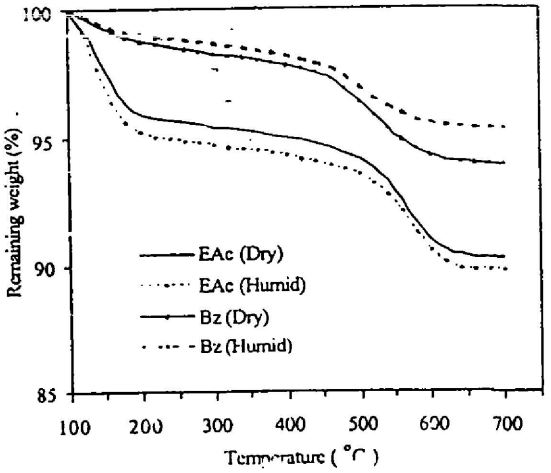

Figure 4. Effect of water on thermogravimetric behaviour of coked Cr-ZSM-5 with ethyl acetate and benzene (Bz). (Coking conditions : Temperature=400°C, GHSV=3,800 hour^{-1}, C_{VOC}=2,000 ppm, C_{H2O}=9,000 ppm in humid feed).

- **Effect of reaction temperature on coke**

Reaction temperature has strong influence on the characteristics and amount of coke accumulated as shown by thermogravimetric oxidation of coke in Figure 5(a) and Figure 5(b). Reaction temperature of 300°C and 400°C for ethyl acetate and benzene, respectively, were identified to cause the highest coke formation and generally, ethyl acetate accumulated more coke than benzene at all reaction temperatures. Low tendency to coking at lower temperatures was due to low activity in this region so that some portion of the feed VOC would pass the reactor unreacted. As evident in the figures, coke formed at 200°C was easily oxidized at between 250°C to 350°C suggesting softer coke with high H/C ratios. At higher reaction temperatures, some softer coke might have decomposed at the condition of its formation leaving behind harder and more carbonaceous fractions with lower H/C ratios. At 200 °C, only softer coke formed and it disappeared above 500°C for the benefit of harder coke fraction for both organics. This observation suggested that as the reaction temperature was increased from 200° to 500°C, coke accumulated on the catalyst gradually changed from polyaromatic hydrocarbon to oxygenated polyaromatic with corresponding increase in the temperature required for its oxidation.

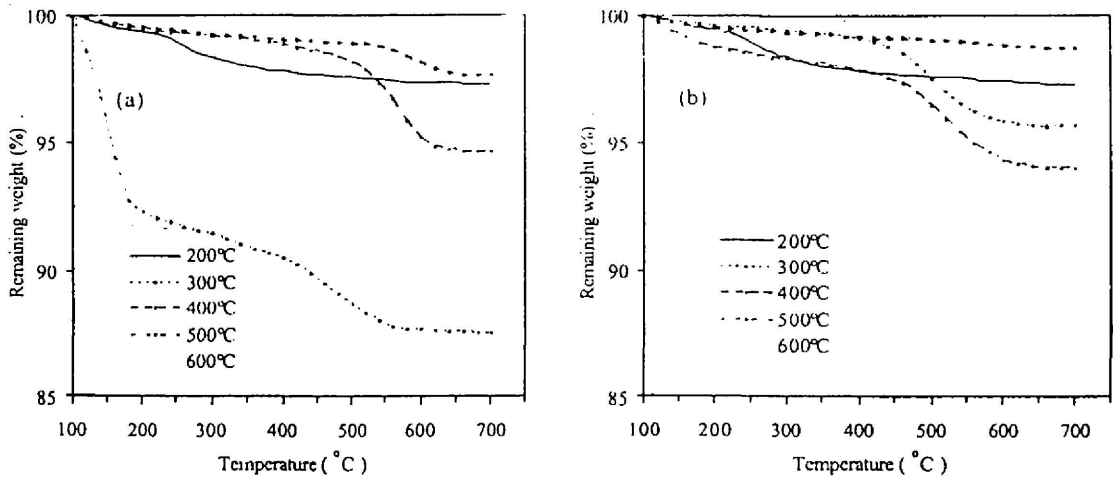

Figure 5. Thermal gravimetry analyses on coked Cr-ZSM-5 obtained at different reaction temperatures. a) Coked with 32,000 ppm ethyl acetate, and, b) coked with 32,000 ppm benzene. (Coking conditions : GHSV=3,800 hour^{-1}, 12 hours).

- Coke Location

Figures 6 show TEM images of fresh and coked Cr-ZSM-5 particles. As can be seen in panel (b) of the figure, a big and rather porous coke particle formed on the catalyst particle. A particle of this size might have formed inside the interparticle macropores of the catalyst rather than in the zeolite micropores. Due to porosity and the location of occurrence, complete blockage of active sites inside the channels of the catalyst was not expected to occur. With micropores constituted about 70% of total surface area to host active sites, the catalyst was expected could maintain most of its activity even after heavily coked as observed experimentally. Active sites would be inaccessible and not available for reaction once complete pore mouth blockage occurred.

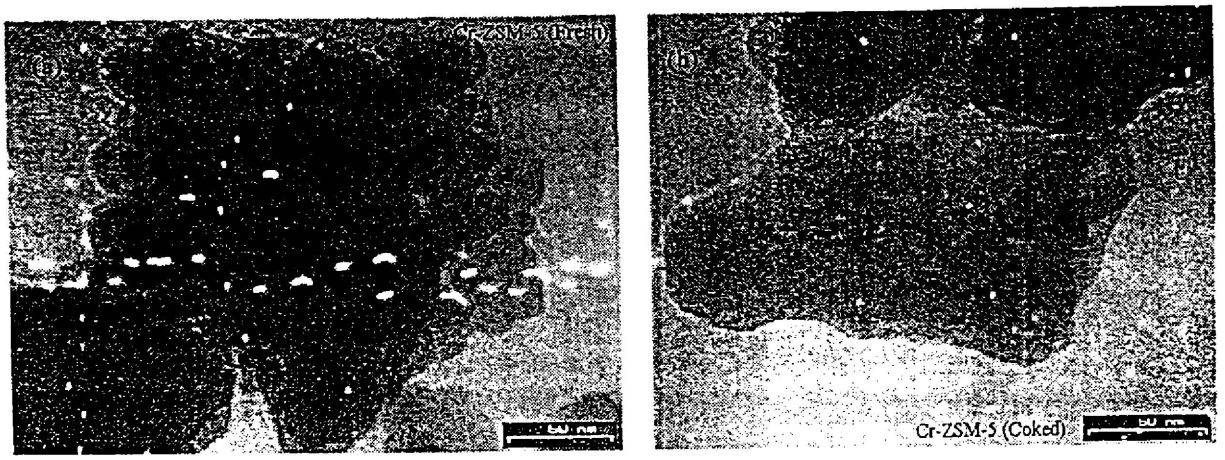

Figure 6. TEM images showing a) fresh Cr-ZSM-5 catalyst, and, b) coke particle formed after reaction with ethyl acetate.

CONCLUSIONS

Coking caused physical and chemical changes on Cr-ZSM-5 catalyst. Elimination of micropores, enlargement of pores and loss of crystallinity of the catalyst of between 65 to 85 % depending on coking conditions were demonstrated. Reduced catalytic activity caused by coking was attributed to partial blocking of active sites. Coke was found to preferentially accumulate around extraframework acid sites and Brønsted acid sites and the rate of coking was found to be faster in dry feed. Water vapour enhanced coke formation from ethyl acetate reaction due to increased surface hydroxyl concentration while with benzene, less coking tendency was demonstrated. Softer coke formed at below 300°C and the difficulty of coke oxidation was further increased as the reaction temperature increased. The stability of Cr-ZSM-5 catalytic activity was due to preference of coke to form in the mesopores of the zeolite rather than in the micropores that host most of active sites.

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